THE EFFECT OF TIME AND TEMPERATURE UPON THE BROMINE ABSORPTION VALUE OF FATS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

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INTRODUCTION

Widely distributed throughout the animal and vegetable kingdoms is found a large group of substances which have one property in common, namely, that they are mainly composed of the radicals of fatty acids, in the main, the higher ones. These substances are known as oils, fats, and waxes. Considered chemically, oils (fatty oils), and fats (solid fats), are the neutral glycerides of fatty acids, whereas waxes are esters formed by the union of fatty acids with alcohols not belonging to the glycerol series. It is noteworthy, however, that this chemical difference does not always find a ready expression in common parlance. The term fat has a definite chemical meaning which restricts its application to a certain number only of the substances of this group and yet many of these substances that are in the strict chemical sense fats, have come to be spoken of as oils, on account of their physical properties, while some are generally known as waxes. The reverse is true in many instances. The term "oil" is somewhat of a misnomer and has no strict chemical significance, being applied not only to liquid fats, but also to substances, such as mineral and essential oils, which are similar to fats in some physical properties but entirely different in constitution.

Many attempts have been made to satisfactorily classify the fats, but the majority have met with little success. The main point of contention seems to be whether the fats shall be classified according to their physical properties, their chemical properties, or on a basis of the plant families from which they are

derived.

The most convenient classification, for practical purposes, appears to be that given by Lewkowitsch,[1] who has arranged them according to the magnitude of their iodine values. His classification is as follows:-

I. Liquid Fats or Fatty Oils

A. Vegetable oils
   1. Drying oils
   2. Semi-drying oils
   3. Non-drying oils

B. Animal oils
   1. Marine animal oils
      (a) Fish oils
      (b) Liver oils
      (c) Blubber oils
   2. Terrestrial animal oils

II. Solid Fats

A. Vegetable fats

B. Animal fats
   1. Body fats
      (a) Drying fats
      (b) Semi-drying fats
      (c) Non-drying fats
   2. Milk fats

Fats and fatty oils consist chiefly of glycerol triesters (commonly known as glycerides), of saturated acids belonging to the fatty series, and of related, unsaturated acids. Glycerol, whose anhydride is the essential and characteristic constituent of all fatty molecules, is a trihydric alcohol. The acids combined with glycerol in edible fats and oils belong in four series, as follows; (1) saturated acids, ($C_nH_{2n}O_2$), (2) unsaturated acids with one double bond, ($C_nH_{2n-2}O_2$) and (3) unsaturated acids with two

double bonds, ($C_nH_{2n-4}O_2$), and also those with three double bonds ($C_nH_{2n-6}O_2$). The properties of the fats themselves depend upon and run parallel with those of the fatty acids, and since this paper is primarily interested in the unsaturated fatty acids it will perhaps be well at this point, to consider, a few of their properties. These acids contain, at some point in the chain, one or more pairs of carbon atoms united by a double bond. This double union may clearly occur, in the higher members of the series, in any one of a number of different positions, and the properites of the acids with a normal chain of a given number of carbon atoms are found to differ with different positions of the double union. The quality of halogen absorption which every member of the unsaturated fatty acid series possesses is dependent entirely upon these double unions. This property is made use of in the separation of mixtures of fatty acids, bromine being the halogen most commonly used. By the addition of bromine to an unsaturated fatty acid, a bromo derivative, or addition product, is formed which is generally a solid and which possesses distinct solubilities. It is this characteristic that is made use of in the separation of a mixture of fatty acids, and which is further applied in the detection of adulterants. Thus linolic acid ($C_{18}H_{32}O_2$) and linolenic acid, $C_{18}H_{30}O_2$, which are found largely in drying and semi-drying oils, on bromination yield the tetrabromide of linolic acid and a hexa-bromide of linolenic acid. Both bromides are solid at ordinary temperatures, and they can be separated by treating the mixture

with ether, when the tetrabromide dissolves, the hexabromide being practically insoluble. Similarly the dibromostearic acid formed from oleic acid is soluble in the ordinary solvents for fats; the tetrabromostearic from linolic acid is only slightly soluble in petroleum ether but dissolves readily in diethyl ether, while the hexabromostearic acid from linolenic acid is almost insoluble in ether but dissolves in hot benzene. A partial separation, at any rate of the bromination products, can be effected by means of these solvents and the composition of a mixture of unsaturated acids approximately ascertained in this way. Thus if the mixed acids have the iodine value 120 and yield no bromination product that is insoluble in ether, i.e. no product with more than four atoms of bromine, it would be safe to conclude in most cases that the mixture was composed of two-thirds oleic acid (Iodine value 90-91) and one-third linolenic acid (Iodine value 181-184).

The "hexabromide test", which is used in commercial analysis, largely for the detection of adulteration of oils, is an application of this principle of separation. For this test[2] 0.3 gram of the liquid fatty acids, or 1 to 2 grams of the unsaponified oil, is dissolved in glacial acetic acid by itself or mixed with ether, and cooled down to 5°C. Bromine is added drop by drop until the color persists. The mixture is allowed to stand at 5°C. for three hours and then filtered through a weighed asbestos filter and the precipitate washed successively with 5 cc. each of cooled acetic acid, alcohol, and ether, and that which remains undissolved is dried and weighed. The insoluble residue

may, in some cases, consist of a mixture of hexabromo and octabromo derivatives. Hexabromostearic acid melts at about 180° C. whereas the octobromide from marine animal oils decomposes at about 200°C. without giving a true melting point. An estimation of the amount of bromine it contains will show this, or the precipitate may be subjected to long extraction with hot benzene. If it does not entirely dissolve in this solvent, the presence of an octobromo derivative is indicated, and its amount may be approximately estimated. The bromination products soluble in ether may similarly, by the use of petroleum ether, be redissolved into their constituents since tetrabromostearic acid dissolves in this solvent only when heated and crystallizes out in needles, almost quantitatively, on cooling. It is obvious from the foregoing that a knowledge of the true bromine absorption value of a given fatty acid or a mixture of fatty acids, would be of great assistance in interpreting the results of a hexabromide test, and would aid materially in the separation of a mixture of fatty acids.

The experimental portion of this paper represents an attempt to determine the conditions necessary for the accurate determination of the bromine absorption values of the oils of the drying, semi-drying, and non-drying series.

HISTORICAL

In about the year 1857 Cailletet[3] communicated to the Societe Industrielle de Mulhouse a titration process for the determination of the bromine absorption value of an unsaturated fatty acid, to be thus performed;"To any given oil add a five per cent aqueous solution of caustic potash and agitate; then pour in excess of a 33 1/2 per cent alcoholic solution of bromine; lastly, add a two per cent solution of turpentine until the color of the free bromine is completely discharged. The turpentine solution is supposed to be known in terms of the bromine solution, and thus the bromine absorption of any oil can be determined. If standard pure oils be at hand, their admixture can be quantitatively ascertained by this means". Cailletet's process had some very obvious disadvantages, according to E. J. Mills[4], the solution of bromine can not be preserved unchanged, probably even for a few hours; and the presence of alcohol and water must inevitably tend to promote oxidation of the oil under treatment. Again, Cailletet admits that the absorption increases in total amount with so moderate a rise of temperature of 10° to 20°C, and that a considerable amount of bromination occurs. It accordingly occurred to Mills[5] (1879-1880), more particularly in connection with hydrocarbon oils, that weak aqueous bromine alone might give gentler and steadier results. This scheme was tried with various samples of petroleum, the sample being agitated with 100 parts of water, and a one-tenth per cent

solution of bromine added, with constant agitation, until KI and starch, used as an external indicator, gave a blue coloration. Under these circumstances constant bromine absorptions were obtained accompanied always with some bromination. The chief difficulty in applying this otherwise satisfactory method consisted in the extreme amount of technique required to obtain uniform measurements. A. H. Allen[6] (1881) subsecuently suggested agitating oils with excess of aqueous sodium hypobromite and hydrochloric acid, and titrating the ultimate free bromine. This amounts to treatment with nascent as well as free bromine in the presence of water; the results are, therefore, of a very composite character. In Mr. Allen's hands this process gave a much less absorption for resin oil than for a shale lubricant, an effect which he and Mills were entirely unable to explain. As it was evidently desirable to confine the absorption to the formation of additive and not substitution products, it was decided to employ CS_2 as the common solvent of the bromine and the substance to be titrated. Water is thus practically excluded and the reaction is marked by great regularity and considerable sharpness. Mills[7] later substituted CCl_4 for CS_2, explaining the change by the fact that at ordinary temperature the solution of bromine is more stable in the former solvent than in the latter. Thus it is to him that we owe the application of the bromine absorption value to the analysis of fats. His method is as follows:- 0.1 grams of an oil of fat, dried thoroughly and filtered, is dissolved in 50 cc. of CCl_4 and placed

in a narrow-mouthed stoppered bottle of 100 cc. capacity. To this solution is added a standard carbon tetrachloride solution of bromine (about 0.006 - 0.008 grams per c.c.) until, after a lapse of fifteen minutes, a coloration persists. The excess of bromine can be measured either by the coloration with that similarly produced in a blank experiment or, more accurately by titrating back with a standard solution of B-napthol in carbon tetrachloride, when monobrome napthol is formed. The bromine absorbed is calculated to 100 grams of fat. The average probable error is stated to be 0.46 per cent.

Mills laid the greatest stress on the necessity of rigidly excluding moisture, since the bromine absorption number is found to be too high in the presence of water; therefore, aqueous solutions of bromine must not be used. Instead of B-napthol, KI may be added, and the liberated iodine titrated with standard sodium thiosulfate.

THEORETICAL

The bromine (or iodine) absorption value is defined as the percentage of bromine (or Iodine) absorbed by the sample. This value is a measure of the proportion of unsaturated fatty acids, which, both in their free state and in combination with glycerol, have the property of assimilating halogens with formation of saturated compounds. Two factors involving the constitution of

the fat, influence the result, (1) the nature of the unsaturated acids present, those with two double bonds absorbing a greater percentage than those with the same number of carbon atoms but with only one double bond, and (2) the molecular weight of the glycerides, those with low molecular weights absorbing a greater percentage than those with the same degree of saturation with high molecular weights. Of these factors the former is by far the most important. For example, linseed oil has very high iodine number (about 175), due to the presence of a considerable amount of linolic acid with two double bonds, while cocoanut oil, which consists largely of saturated acids, has a very low number (less than 10). Theoretically, the acids belonging to the oleic and ricinoleic series should absorb two atoms of bromine or iodine or one molecule of iodine chloride. Hence the glycerides of these acids should absorb six atoms of bromine or iodine, or three molecules of iodine chloride. Similarly the acids of the linolic series should assimilate four atoms of halogens or two molecules of iodine chloride; the members of the linolenic series; six atoms of halogens or three molecules of iodine chloride, etc. While these theoretical postulates are born out by experiments in the case of oleic, ricinoleic, linolic, chaulmoogric, linolenic, clupanodonic acids, it appears that this rule only applies to doubly linked carbon atoms. Trebly linked carbon atoms should, theoretically, absorb with equal facility four atoms of bromine or iodine, or two molecules of iodine chloride. Experience has shown however, that only two atoms are readily absorbed. In the case

of chlorine and bromine two molecules can be added by allowing the action to last a prolonged time, especially if this action be assisted by catalysts,(i.e. ferric chloride, etc.) and exposure to light. In the case of iodine and iodine chloride, only one molecule of halogen is absorbed. This behavior would seem to constitute a most characteristic means of differentiating the acids of the linolic series from the isomeric acids of the stearoic series. It is evident that the preparation of products containing chlorine absorbed solely by the process of addition is attended with more difficulty than that of bromo-, iodo-, or iodochloro, addition products; hence in technical analysis only bromine and iodine, the latter in the form of iodine chloride, are employed.

If dry bromine is allowed to act on an oil it is absorbed with a more or less violent reaction, and evolution of hydrobromic acid takes place. The reaction must, therefore, be moderated by previously dissolving both the bromine and the oil in a suitable solvent. Carbon tetrachloride, as first employed by Mills[8] is generally employed as the solvent. In the course of the reaction, even when carbon tetrachloride is used as the solvent, small quantities of hydrobromic acid are formed, due to the substitution of hydrogen by bromine in the molecule of the fatty substance. The hydrobromic acid thus formed can readily be detected by shaking the product with water and testing the aqueous solution with silver nitrate. It is, therefore, evident that concurrently with addition, i.e. the absorption of bromine due to

bromine being assimilated by one molecule of an unsaturated glyceride to form a saturated compound, a further quantity of free bromine disappears, due to the formation of substitution products and hence of hydrobromic acid; therefore, the total absorption of bromine is due to both addition and substitution. Since greater amounts of substitution products are formed with more concentrated bromine solutions, it is advisable to use moderately dilute solutions of bromine. It is further evident from the above that absorption values obtained by allowing dry bromine to act on oils are very apt to be too high. The amount of substitution taking place can be ascertained by a measure of the hydrobromic acid formed and the true bromine absorption value will, therefore, be the total absorption value minus the bromine absorbed by substitution.

McIlhiney[9] (1894) determines the bromine addition and the bromine substitution values in the following manner:-[10] from 0.25 to 1 gram of the oil or fat is dissolved in 10 cc. of carbon tetrachloride in a 500 cc. stoppered bottle and an excess of a one-third normal solution of bromine in carbon tetrachloride is added. After a few minutes the bottle is placed in ice, thus producing a partial vacuum by the condensation of the vapors. A piece of india rubber tubing is now slipped over the neck in such a way as to form a well around the stopper. The well is filled with water, which is sucked into the bottle by carefully lifting the stopper. Then 25 cc. of water are introduced into the bottle, the contents are well shaken (to effect complete absorption of the hydrobromic acid), and ten to twenty cc. of a 20 per cent

solution of potassium iodide and about 75 cc. more water are added. The iodine liberated by the excess of bromine is measured by titration with standard thiosulphate solution and calculated to bromine. The total amount of bromine added is ascertained in a blank test, and the difference between the two amounts corresponds to the total bromine absorption. This is calculated to units in per cent of the sample taken. The contents of the bottle are next transferred to a separating funnel and the aqueous solution is separated and filtered. If the filtrate is blue, it is decolorized by a few drops of thiosulphate solution, and the free acid is determined as hydrobromic acid by titration with decinormal alkali, methyl orange being used as an indicator. The bromine calculated from the hydrobromic acid and expressed in per cent of the sample gives the bromine substitution value. Twice this number subtracted from the total bromine absorption value furnishes the bromine addition number. It is obvious that the substitution number must be doubled since for each bromine atom converted into hydrobromic acid there has been removed from the original bromine solution one molecule (or two atoms of bromine), as is explained by the following equation:-

$$C_nH_mO_2 + Br_2 = C_nH_{m-1}O_2Br + HBr$$

In order to have a standard measure of the accuracy of the experimental portion of this paper, the iodine values of the oils under examination were determined. As a matter of fact, in commercial work of today, the determination of the iodine absorpt-

ion value has wholly superseded the determination of the bromine absorption value, as a measure of the unsaturation of an oil. There are at the present time, three methods which are most commonly used for the determination of the iodine absorption value, i.e., those of Hübl, Wijs. and Hanus, the last two being modifications of the former. Hübl[11] found that iodine is but slowly assimilated by oils and fats at the ordinary temperature of a room, while at higher temperatures[12] the action of iodine becomes very irregular owing to the occurence of a series of complicated reactions. He ascertained, however, that from an alcoholic solution of iodine, in the presence of mercury bichloride, glycerides of the unsaturated fatty acids absorb iodine in a very regular, well defined manner, so that a quantitative method can be based on this reaction. His method[13] consists essentially in adding 50 cc. of the iodine solution (consisting of a mixture of 26 gms. of pure iodine in 500 cc. of 95% alcohol (mixed at least 12 hours before using) to the sample, which is dissolved in pure chloroform, in a special Erlenmeyer flask. The flask is tightly stoppered and the gutter around the stopper is filled with a 15 per cent solution of potassium iodide, the flask shaken gently and allowed to stand in a cool dark place for three hours, a blank determination being made at the same time, using exactly the same amounts of the same reagents. At the end of three hours the flask is carefully unstoppered, 20 cc. more of the potassium iodide solution added and the contents titrated with thiosulphate. The absorbed iodine is

calculated in terms of percentage of the weight of the original sample.

Hübl's method has been examined by many chemists and has proven to be one of the most valuable methods employed in the technical analysis of oils, fats, and waxes. Long before a comprehensive explanation was found for the reactions taking place in this ingenious process, the numbers obtained by this method afforded the most valuable guidance in the examination of fats and oils. Hübl himself explained the reaction by assuming that a chloro-iodo-addition compound was formed, for he had obtained from oleic acid a saturated fatty substance to which he assigned the formula $C_{18}H_{34}ClIO_2$.

If Hübl's view is correct, then theory requires, in the first instance, that saturated fatty acids should have no iodine value, and secondly, that pure unsaturated fatty acids should furnish iodine values agreeing with the theoretical numbers. Lewkowitsch[14] has proven the first case to be true, and obtained a close agreement to the second case in a large number of instances, but he also obtained values with a number of fatty acids which did not agree with the theoretical. From his results, Lewkowitsch concluded[15] that it is the position of the double bond in the unsaturated acid that influence the iodine absorption. If the double bond is distant from the carboxyl group, as in ordinary oleic acid, the iodine value is normal, while if it is nearer the carboxyl group, as in the case of undecylenic, crotonic and fumaric acids, the iodine value is lower than the theoretical

value. It would, therefore, appear that the determination of the iodine value would furnish a means of drawing some conclusions as to the position of the double bond in an unsaturated acid. Lewkowitsch further confirmed the fact that all glycerides and fatty acids which occur in commercial oils, fats and waxes, do conform with theory if treated with Hübl's iodine solution according to the directions given.

Ephraim[16] made the next important step in the scientific explanation of the Hübl reaction. He observed that the Hübl solution required a much larger amount of sodium thiosulphate after addition of potassium iodide than it did without it, and from this he concluded that on mixing the components of the solution there is formed at once a substance capable of liberating iodine from potassium iodide. He expressed the chemical change taking place in the iodine solution by the following reaction:-

$$Hg\ Cl_2 + I_2 = HgClI + ICl$$

This equation would correspond to Hübl's directions, that for two atoms of iodine at least 1 molecule of mercuric chloride must be used. Ephraim, therefore, concluded that a solution of iodine monochloride could be used in the place of Hübl's solution; and a number of experiments carried out with such a solution furnished results identical with those obtained by the use of Hübl's solution. Experiments by Wijs[17] led to a satisfactory explanation of the reactions occuring in the Hübl solution, and the subsequent

confirmation of the views held by Ephraim. The first change taking place on mixing the solutions of iodine and mercuric chloride is represented by the following equation:-

$$HgCl_2 + 2I_2 = HgI_2 + 2ICl \qquad (1)$$

It is yet an open question whether the action takes place in two stages, or not, as represented by the two equations

$$HgCl_2 + I_2 = HgICl + ICl$$
$$HgClI + I_2 = HgI_2 + ICl$$

The iodine chloride (ICl) formed, reacts with the water contained in the 95 per cent alcohol in the following manner:-

$$ICl + H_2O = HCl + HIO \qquad (2)$$

but this soon reaches a limit, since the hydrochloric acid thus formed precludes the complete decomposition of the water present. The hypoiodous acid (IOH) is converted into iodic acid and free iodine, thus:-

$$5IOH = IO_3H + 2H_2O + 4I \qquad (3)$$

although this occurs very slowly, for the amount of hypoiodous acid is, as shown, a limited one. Since, however, the iodic acid will interact with free iodine and the hydrochloric acid (equation 2) in the solution, to form iodochloride (ICI), in the manner expressed by the equation:

$$IO_3H + 4I + 5HCl = 5ICl + 3H_2O \qquad (4)$$

it will be easily seen that a complicated system of equilibrium will result, the chief components of which are represented by the equation (2). We can then assume in the Hübl solution the presence of the following substances:-

$HgCl_2$, HgI_2, I, ICI, HCl, IOH, and IO_3H.

On standardizing the solution of iodine, potassium iodide solution and water are added. The changes then taking place are expressed by the following equations:-

$$ICl + KI = KCl + I_2 \qquad (5)$$

$$HCl + IOH + KI = KCl + H_2O + I_2 \qquad (6)$$

$$IO_3H + 5HCl + 5KI = 5KCl + 3H_2O + 3I_2 \qquad (7)$$

It will thus be seen that, provided no other reaction has taken place, the total amount of iodine originally employed (when preparing the iodine solution) must be found in the blank test as iodine, and further, that the final solution can not contain free acid, if the alcohol used was neutral.

Wijs assumed that the active principle in the iodine solution of Hübl is hypoiodous acid and not iodine monochloride. In support of his argument he quotes the following three arguments: (1) If iodine monochloride was the active substance, the halogen should be absorbed more rapidly from Waller's solution[18] (in which 25 gms. of HCl are added to Hübl's solution) than from Hübl's solution, since iodochloride is present in greater concentration

in the former solution than in the latter. But the reverse is actually the case, and this may be explained by the gradual or retarded formation of hypoiodous acid. (2) When a solution of hypoiodous acid (prepared by shaking an alcoholic iodine solution with freshly precipitated mercuric oxide and filtering off) is mixed with an oil, values identical with the Hübl iodine numbers are obtained, the absorption being complete after ten seconds (one experiment only is given). (3) On increasing the concentration of hypoiodous acid through the addition of iodine, mercuric chloride and water (which favor the formation of hypoiodous acid), more rapid absorption takes place, whereas it is retarded by those agents which reduce the hypoiodous acid concentration, i.e., mercuric chloride and hydrochloric acid. If Wijs' assumption was correct, there should be formed for each molecule of hypoiodous acid which is absorbed by an oil, one molecule of hydrochloric acid. Although some acid is found, by no means the full quantity is obtained; therefore, Wijs is driven to the further, somewhat forced assumption that, taking oleic acid as an example, the reaction proceeds as follows:-

$$C_{18}H_{34}O_2 + HIO = C_{18}H_{34}O_2\ IOH$$

$$C_{18}H_{34}O_2 + HCl = C_{18}H_{34}O_2\ ICl + H_2O$$

It is evident that the final product is the same as would be obtained by assuming that iodochloride is the active substance, and that iodochloride is absorbed as such. In fact, Wijs' proposal to substitute for Hübl's solution a solution of iodine monochloride

in glacial acetic acid (inasmuch as the preparation and keeping of a solution of hypoiodous acid would offer almost insuperable difficulties), amounts practically to a tacit acceptance of the view that iodochloride is the active agent. Wijs' method differs from that of Hübl's only in that his iodine solution is prepared by dissolving separately 12.5 to 13 gms. iodine in a liter of glacial acetic acid and then adding chlorine gas until all is converted to iodine chloride (ICl).

The foregoing explanations show that Hübl has hit off in a very ingenious manner the conditions most favorable for obtaining iodine values which are in close agreement with theory. It is, therefore, possible, if a sample contains the glyceride of one unsaturated fatty acid of known composition in admixture with glycerides of saturated fatty acids, to calculate the absolute amount of glyceride of that unsaturated fatty acid.

Hanus[19] later suggested that Wijs' method be modified by the use of iodine bromide in place of iodine chloride. Hanus' method was adopted by the Association of Official Agricultural Chemists in 1905 and is in use to-day in practically all modern laboratories. In this method the fat or oil is dissolved in 10 cc. of chloroform and 25 cc. of the iodine solution is added, and the mixture allowed to stand for 30 minutes, with occasional shaking. The excess of iodine should be at least 60% of the amount added. After 30 minutes, 10 cc. of a 15% solution of potassium iodide and 100 cc. of distilled water are added to the contents of the

bottle and the bottle shaken thoroughly. The excess of iodine is then titrated with thiosulphate (decinormal) until the yellow color of the solution has almost disappeared. A few drops of starch paste are then added and the titration continued until the blue color just disappears. Toward the end of the reaction the bottle is stoppered tightly and shaken violently, in order that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution. The Hanus method gives results which agree quite closely with those obtained by Hübl's method, while Tolman and Munson[20] in an extended comparison of the three methods almost invariably obtained results with the Wijs method which were higher than those obtained by the other two. The method of Hübl is "official" in the United States, but that of Hanus has been adopted by the Association of Official Agricultural Chemists as an optional method for the examination of edible oils and fats. The method of Wijs is more commonly used in England and is recommended in preference to the Hanus method by Lewkowitsch[21] and Archbutt.[22]

EXPERIMENTAL

The oils used for the experimental work of this paper were almond oil, cottonseed oil, corn or maize oil and linseed oil, selected as being representative of the three classes of vegetable oils, i.e., non-drying, semi-drying and drying oils.

Almond oil, which is representative of the non-drying oils, is obtained from the seeds of the Prunus Amyg Dalas. The commercial product is obtained by expression or extraction from bitter almonds, of the variety Amara. Almond oil is free from stearin, its glycerides consisting chiefly of olein. Its high iodine value, however, points to the presence of glycerides of fatty acids belonging to a less saturated series than the oleic series. Indeed, Farnsteiner[23] has isolated linolic tetrabromide from the mixed fatty acids in a quantity corresponding to 5.79% of linolic acid.

Cottonseed oil is representative of the semi-drying oils and is found in the seeds of the various kinds of cotton plants, the species cultivated in the United States being Gossypium hirsutum, L. It contains chiefly:- as solid fatty acids, palamitic and some arachidic; as liquid fatty acids, oleic and linolic. No ether soluble bromides have been obtained from cotton-seed oil. Linolenic acid may be considered absent. From the isolated linolic tetrabromide in the mixed fatty acids, Farn-steiner found an amount corresponding to 18.45% linolic acid.

Corn oil is also representative of the semi-drying oils and it is obtained from the germ of the maize plant. Zea mays, L. It contains the liquid fatty acids, oleic and linolic.

Linseed oil is representative of the drying oils and is obtained from the seeds of flax plants, Linum usitatissimum, L. Its chemical composition is imperfectly known, but it has been shown to contain the following liquid glycerides:* oleic, linolic, linolenic and isolinolenic acids.

The solutions used in the determination of the bromine absorption values were prepared as follows:-

(1) Standard potassium permanganate, used for the standardization of the thiosulphate solution. The potassium permanganate was standardized against chemically pure Mohr's salt (ferrous ammonium sulphate) in the following manner:- The sample was weighed into a 300 cc. Erlenmeyer flask, and a half spoonful of sodium carbonate added. 25 cc. of hot dilute sulphuric acid were than added, the carbon dioxide thus generated forcing the air from the flask, preventing any oxidation of the ferrous salt. To the solution was added 50 to 100 cc. of hot water and the solution was titrated at once with the permanganate solution. The results were as follows:-

	#1	#2	#3	#4
Wt. of sample	0.4072	0.4466	0.3505	0.2488
c. c. $KMnO_4$	9.15	9.95	7.85	5.60
N. F. $KMnO_4$	0.1134	0.1130	0.1132	0.1133

Average normality factor = 0.1133

(2) Sodium thiosulphate, standardized against the potassium permanganate solution in the following manner:- Approximately 1 gram of potassium iodide was placed in a glass-stoppered bottle, 10 c. c. of water were added and after the potassium iodide had completely dissolved 10 c. c. of the standard permanganate were added from a standardized pipette. 10 c.c. of dilute hydrochloric acid were then added and the solution allowed to stand for five minutes, at the end of which time 100 c.c. of water were added and the solution titrated with the sodium thiosulphate.

	#1	#2	#3	#4
c.c.$KMnO_4$	10	10	10	10
c.c.$Na_2S_2O_3$	11.54	11.55	11.55	11.55
N.F.$Na_2S_2O_3$	0.09809	0.09809	0.09809	0.09809

Average normality factor = 0.09809

(3) Bromine solution, prepared by diluting 6 c.c. or approximately 18 gms. bromine to 1 liter with carbon tetrachloride.

(4) Potassium iodide - 150 gms. per liter of water.

(5) Starch solution was prepared by gently boiling, for 10 minutes, 1 gm. of soluble starch with 200 c.c. water. A

fresh solution of starch was prepared for each day a run was made.

The following solutions were used for the determinations of the iodine values:-

(6) Iodine solution - 13.2 grms. iodine were dissolved in 1000 c.c. of glacial acetic acid (99.5%) (which showed no reduction with bichromate and sulphuric acid). Enough bromine was added to double the halogen content.

(7) The other solutions used for determining the iodine numbers have been described above.

In order to establish a standard for the determined bromine absorption values, the iodine values of the four oils were first determined, using the Hanus method which has been described under the theoretical discussion. No trouble was encountered in establishing satisfactory checks on the results of these determinations.

ALMOND OIL	# 1	#2
Wt. sample + container	36.2674	35.3961
Wt. " - sample	35.6402	35.1667
Wt. Sample	.6272	.2294
c.c. Hanus solution	50.	25.
c.c. $Na_2S_2O_3$	55.55	34.56
IODINE VALUE	97.96	97.97

Blank - 25 c.c. Hanus solution required - 52.45 c.c. thiosulphate.

COTTONSEED OIL

Wt. sample	0.1453	0.1379
c.c. Hanus solution	25.	25.
c.c. thiosulphate	39.36	39.95
IODINE VALUE	106.17	106.29

Blank - 25 c.c. Hanus solution required - 51.73 c.c. thiosulphate.

CORN OIL

Wt. sample	.2764	.2700
c.c. Hanus solution	25.	25.
c.c. thiosulphate	25.72	26.55
IODINE VALUE	116.00	116.00

Blank - 25 c.c. Hanus solution required - 51.73 c.c. thiosulphate.

LINSEED OIL

Wt. sample	.2486	.2541
c.c. Hanus solution	25.	25.
c.c. thiosulphate	17.1	16.3
IODINE VALUE	171.87	171.95

Blank - 25 c.c. Hanus solution required - 51.40 c.c. thiosulphate.

The bromine absorption values of the oils were obtained as follows:- 0.2 - 0.35 gram of oil was weighed into a glass stoppered Erlenmeyer flask - 10 c.c. carbon tetrachloride were added to dissolve the oil, and then 25 c.c. of the bromine

solution were added, and the flask placed under varying conditions as described below. A blank was prepared for each group of four samples and treated exactly in the same manner as the samples. At the end of the specified time, 15 c.c. of a 15 per cent solution of potassium iodide and 100 c.c. of water were added and the liberated iodine titrated at once with thiosulphate. Near the end of the reaction starch was added as an indicator.

After one acquires the necessary technique, this titration is a very accurate and a very beautiful one, the end point being easily discerned, with a little care and practice. Considerable shaking is often necessary to insure complete absorption of all the bromine in the carbon tetrachloride layer by the aqueous potassium iodide portion, and care must be exercised to prevent the loss of any portion of the aqueous layer through a loose stopper or through too violent shaking. At first the analyst is apt to be confused by the succession of colors which results after the addition of the starch indicator, but since the final reaction yields a colorless mixture, there should be no confusion in regard to the true end point. The following succession of colors may be noticed in the aqueous layer after the addition of the indicator:- deep blue black, dark blue, dark olive green, light olive green, light green, purple, lavender, very light lavender, and finally colorless. The color of the carbon tetrachloride layer usually goes from a dark lavender to a light lavender to colorless, after the addition of the indicator.

The analyst should take precautions not to titrate to a colorless aqueous layer before adding the indicator, for in such a case he is very apt to find, after shaking the flask vigorously, that he has passed the end point. After the starch has been added to the mixture, the thiosulphate should be added cautiously, two or three drops at a time, each addition being followed by a vigorous shaking, until a very light lavender color appears, after which it requires but a drop or two to complete the reaction. The analyst must also be certain, before starting the titration, that an excess of potassium iodide is present, for in the absence of an excess low results are obtained.

After titrating the liberated iodine, and thereby ascertaining the bromine absorption value, the contents of the flask were transferred to a separatory funnel and the carbon tetrachloride layer separated from the aqueous layer. The aqueous layer was then titrated with fiftieth normal sodium hydroxide, using methyl orange as indicator, and the amount of hydrobromic acid formed during the reaction thus measured. From the amount of hydrobromic acid formed was calculated the amount of substitution which had occurred.

In order to study the conditions necessary for the most accurate determination of the bromine absorption value, as compared with the iodine value, determinations were made at three different temperatures, varying the time with each temperature in the following series:- 30 minutes, 1 hour, 2 hours, 4 hours, 8 hours, 16 hours and 24 hours. The temperatures were 20°C., 0°C., and -10°C.

The temperatures were kept constant in each case. At 20°C., this was accomplished by means of constant temperature incubator, regulated by an electric thermo-couple, while at 0°C., it was accomplished by means of a heavily insulated box, in which the samples were surrounded by ice. The same box was employed to obtain a temperature of -10 0°C., using salt to lower the temperature of the ice.

The results obtained from the determinations were calculated to the percentage of bromine absorbed, or the number of grams of bromine which 100 grams of the fat would absorb. Example of a determination and the calculations involved:-

ALMOND OIL	#1	#2
Wt. sample + wt. container	31.8746	31.3816
Wt. container - sample	31.6256	31.1368
Wt. sample	00.2490	00.2448
c.c. bromine solution	25.	25.
c.c. $Na_2S_2O_3$	36.3	36.6
Time	1 hour	1 hour
Temperature	0°C.	0° C.
Bromine value	61.12	61.24

Blank - 25 c.c. Bromine solution required 55.7 c.c. thiosulphate.

Then, in the case of #1 for example, 55.7 - 36.3 = 19.4, or 19.4 represents the c.c. of N/.09809 bromine absorbed by .2490 gm. of almond oil, (0.09809 being the normality factor of the $Na_2S_2O_3$). 1 c.c. of normal bromine weighs 0.07992. It is, there-

fore, evident that the following expression will give the bromine value:-

$$\frac{19.4 \times 0.09809 \times .07992}{.2940} = 61.12,$$ the bromine absorption value of almond oil, standing in contact with bromine for 1 hour at 0°C.

RESULTS

The following tables represent the results obtained, by varying the time and temperature; and the appended curves present the same in a graphical form,- the mean of two check determinations being used for each co-ordinate point:-
(See following pages).

Table 1.

Almond Oil
Iodine value =97.96
Calculated bromine value =61.72

Temperature	Time	Bromine value	Mean	Acidity per 0.1 gm. of sample	Grams of substituted Br. per 0.2 gm. sample
20° C	30 min.	58.78		.0451	.0890
"	30 "	58.61	58.695	.0437	.0862
"	1 hour	59.36		.0387	.0764
"	1 "	59.46	59.41	.0377	.0744
"	2 "	61.05		.00632	.008648
"	2 "	61.00	61.025	.00420	.00830
"	4 "	61.20		.0462	.0910
"	4 "	61.26	61.23	.0454	.090
"	8 "	61.25		.0444	.0876
"	8 "	61.20	61.225	.0437	.0860
"	16 "	61.70			
"	16 "	61.50	61.60		
"	24 "	63.12		.0687	.136
"	24 "	63.22	63.17	.0553	.1096
0° C	30 min.	60.61			
"	30 "	60.70	60.655		
"	1 hour	61.12			
"	1 "	61.14	61.13		
"	2 "	61.18			
"	2 "	61.06	61.12		
"	4 "	61.27			
"	4 "	61.12	61.195		
"	8 "	61.40			
"	8 "	61.29	61.345		
"	16 "	61.36			
"	16 "	61.27	61.315		
"	24 "	61.40			
"	24 "	61.24	61.32		
-10° C	30 min.	61.19		.0151	.0294
"	30 "	61.04	61.115	.01405	.0276
"	1 hour	61.40		.0174	.0344
"	1 "	61.35	61.375	.02005	.0394
"	2 "	61.63		.0364	.072
"	2 "	61.60	61.615	.0369	.0728
"	4 "	61.62		.0159	.0314
"	4 "	61.59	61.605	.0152	.0300
"	8 "	61.64		.0167	.0330
"	8 "	61.72	61.68	.0163	.0322
"	16 "	61.98		.01355	.0268
"	16 "	61.89	61.935	.01371	.0270
"	24	62.26		.0182	.0360
"	24 "	62.20	62.23	.0217	.0428

Table II.

Cottonseed Oil
Iodine value = 106.23
Calculated bromine value = 66.8

Temperature	Time	Bromine Value	Mean	Acidity per 0.1 gm. of sample	Grams of substituted Br. per 0.2 gm. sample
20° C	30 min.	62.94		.0411	.0810
"	30 "	63.10	63.02	.0410	.0810
"	1 hour	63.69		.0400	.0790
"	1 "	63.62	63.655	.0374	.0740
"	2 "	65.13		.0108	.0213
"	2 "	65.10	65.115	.01095	.0214
"	4 "	65.32		.0410	.0810
"	4 "	65.47	65.395	.0396	.0780
"	8 "	65.90		.0422	.083
"	8 "	65.77	65.835	.04335	.0854
"	16 "	66.40			
"	16 "	66.28	66.34		
"	24 "	67.76		.014	.0276
"	24 "	67.81	67.785	.0133	.0262
0° C	30 min.	65.30			
"	30 "	65.20	65.25		
"	1 hour	64.60			
"	1 "	64.60	64.60		
"	2 "	65.48			
"	2 "	65.41	65.445		
"	4 "	65.45			
"	4 "	65.24	65.345		
"	8 "	65.68			
"	8 "	65.62	65.65		
"	16 "	65.57			
"	16 "	65.49	65.53		
"	24 "	65.60			
"	24 "	65.70	65.65		
-10°	30 min.	65.54		.01930	.038
"	30 "	65.62	65.58	.01945	.0384
"	1 hour	65.75		.0224	.0442
"	1 "	65.59	65.67	.0199	.0392
"	2 "	65.63		.0485	.0956
"	2 "	65.50	65.565	.04415	.0870
"	4 "	65.83		.01705	.0336
"	4 "	65.70	65.765	.01615	.0318
"	8 "	65.81		.0161	.0317
"	8 "	65.65	65.73	.0155	.0306
"	16 "	65.18		.0175	.0346
"	16 "	66.22	66.20	.01785	.0352
"	24 "	66.20		.0144	.0284
"	24 "	66.14	66.17	.0140	.0276

Table III.

Corn Oil
Iodine value = 116.0
Calculated bromine value = 72.92

Temperature	Time	Bromine value	Mean	Acidity per 0.1 gm. of sample	Grams of substituted Br. per 0.2 gm. sample
20° C	30 min.	70.95		.0451	.0890
"	30 "	71.05	71.0	.0437	.0864
"	1 hour	71.32		.0414	.0816
"	1 "	71.18	71.25	.0413	.0815
"	2 "	71.47		.00186	.0366
"	2 "	71.36	71.415	.00207	.0408
"	4 "	71.65		.0373	.0736
"	4 "	71.71	71.68	.0381	.0752
"	8 "	71.96		.0432	.0850
"	8 "	71.78	71.87	.0416	.082
"	16 "	71.82			
"	16 "	72.96	71.89		
"	24 "	72.80		.00201	.00396
"	24 "	72.90	72.85	.00187	.00368
0° C	30 min.	71.40			
"	30 min.	71.42	71.41		
"	1 hour	71.70			
"	1 "	71.61	71.655		
"	2 "	71.56			
"	2 "	71.60	71.58		
"	4 "	71.65			
"	4 "	71.63	71.64		
"	8 "	71.70			
"	8 "	71.54	71.62		
"	16 "	71.77			
"	16 "	71.61	71.69		
"	24 "	71.70			
"	24 "	71.72	71.71		
-10° C	30 min.	70.71		.0027	.00532
"	30 "	70.84	70.775	.00261	.00516
"	1 hour	71.82		.00278	.00548
"	1 "	71.64	71.73	.00350	.00692
"	2 "	71.75		.03965	.078
"	2 "	71.81	71.78	.03830	.0756
"	4 "	71.83		.01235	.0244
"	4 "	71.89	71.86	.0117	.0230
"	8 "	71.77		.0119	.0234
"	8 "	71.94	71.855	.01007	.0198
"	16 "	71.92		.0145	.0286
"	16 "	71.86	71.89	.0144	.0284
"	24 "	71.85		.0145	.0286
"	24 "	71.76	71.805	.0155	.0306

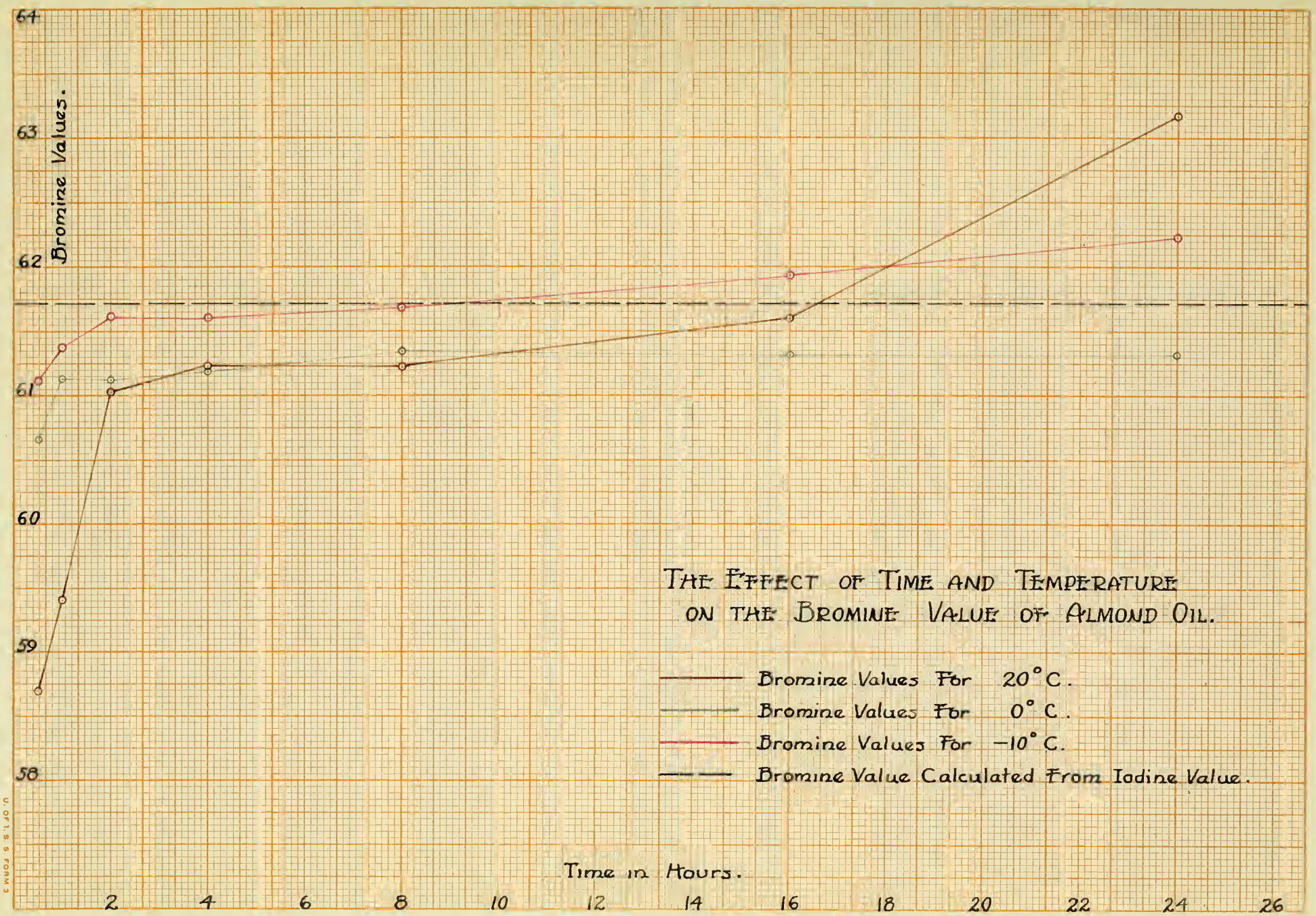
Table IV.

Linseed Oil

Iodine Value = 171.91

Calculated bromine value = 108.24

Temperature	Time	Bromine value	Mean	Acidity per 0.1 gm. of sample	Grams of substituted Br. per 0.2 gm. sample
20° C	30 min.	96.68		.037	.0730
"	30 "	96.82	96.75	.0299	.0590
"	1 hour	98.76		.0300	.0590
"	1 "	98.88	98.82	.0305	.0602
"	2 "	100.53		.0127	.0251
"	2 "	100.52	100.525	.0105	.0208
"	4 "	102.40		.0384	.0758
"	4 "	102.58	102.49	.0364	.072
"	8 "	105.97		.0363	.0718
"	8 "	105.82	105.895	.0359	.0710
"	16 "	109.20			
"	16 "	109.28	109.24		
"	24 "	110.20		.0191	.0378
"	24 "	110.07	110.135	.0173	.0342
0° C	30 min.	95.90	95.87		
"	30 "	95.84	95.87		
"	1 hour	95.91			
"	1 "	95.84	95.875		
"	2 "	104.31			
"	2 "	104.19	104.25		
"	4 "	105.88			
"	4 "	105.76	105.82		
"	8 "	106.51			
"	8 "	106.42	106.365		
"	16 "	106.79			
"	16 "	106.42	106.605		
"	24 "	107.62			
"	24 "	107.56	107.59		
-10° C	30 min.	92.36		.002075	.0041
"	30 "	92.22	92.29	.00233	.0046
"	1 hour	95.50		.00393	.00776
"	1 "	95.62	95.56	.00242	.00478
"	2 "	101.16		.03515	.0692
"	2 "	101.30	101.23	.03635	.0716
"	4 "	101.84		.00861	.0170
"	4 "	101.95	101.895	.00905	.0179
"	8 "	103.90		.01009	.0200
"	8 "	103.75	103.825	.01120	.0221
"	16 "	104.87		.00430	.00850
"	16 "	104.77	104.82	.00443	.00876
"	24 "	105.55		.01405	.0278
"	24 "	105.39	105.47	.01440	.0284


64
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58
Bromine Values.
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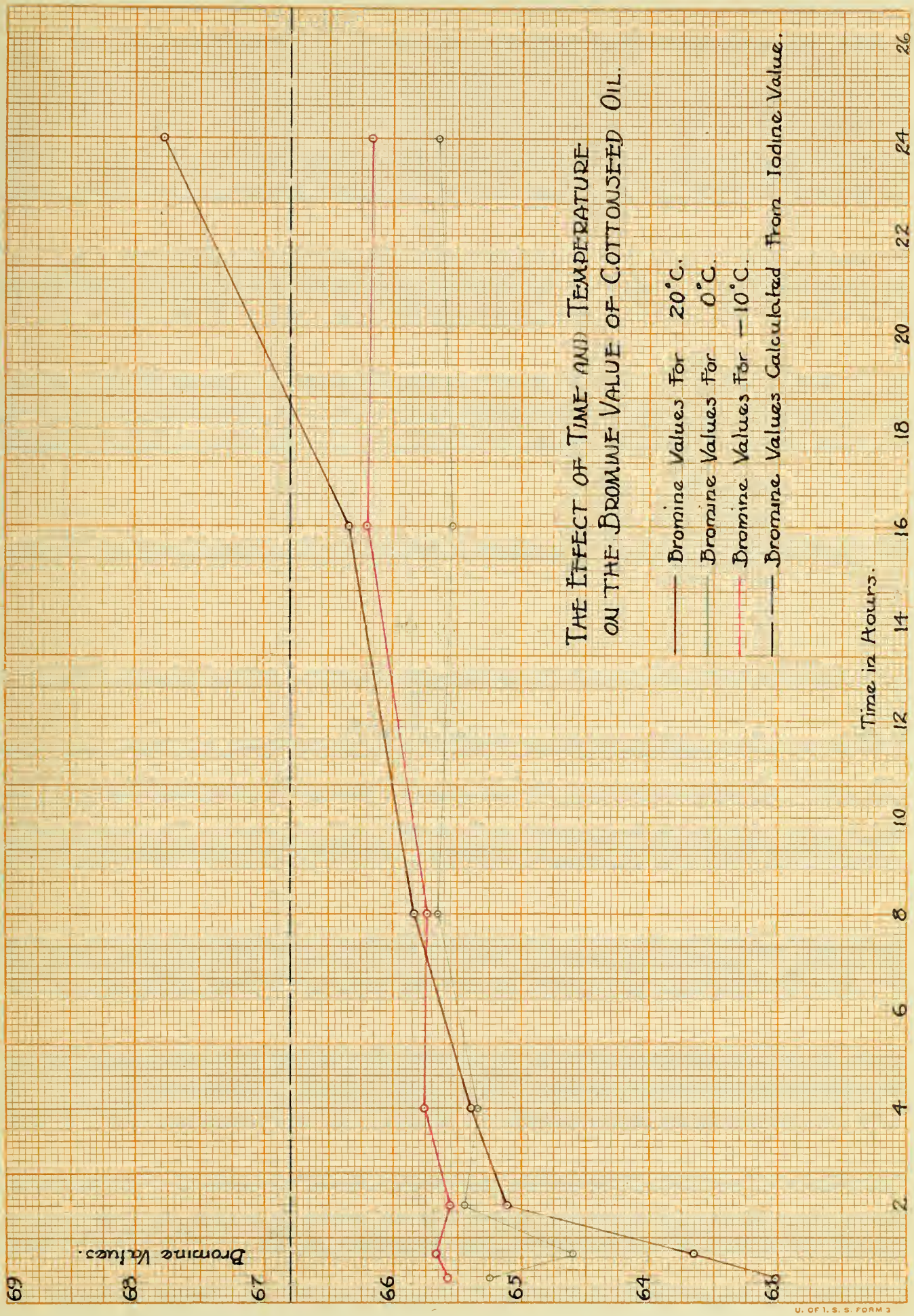
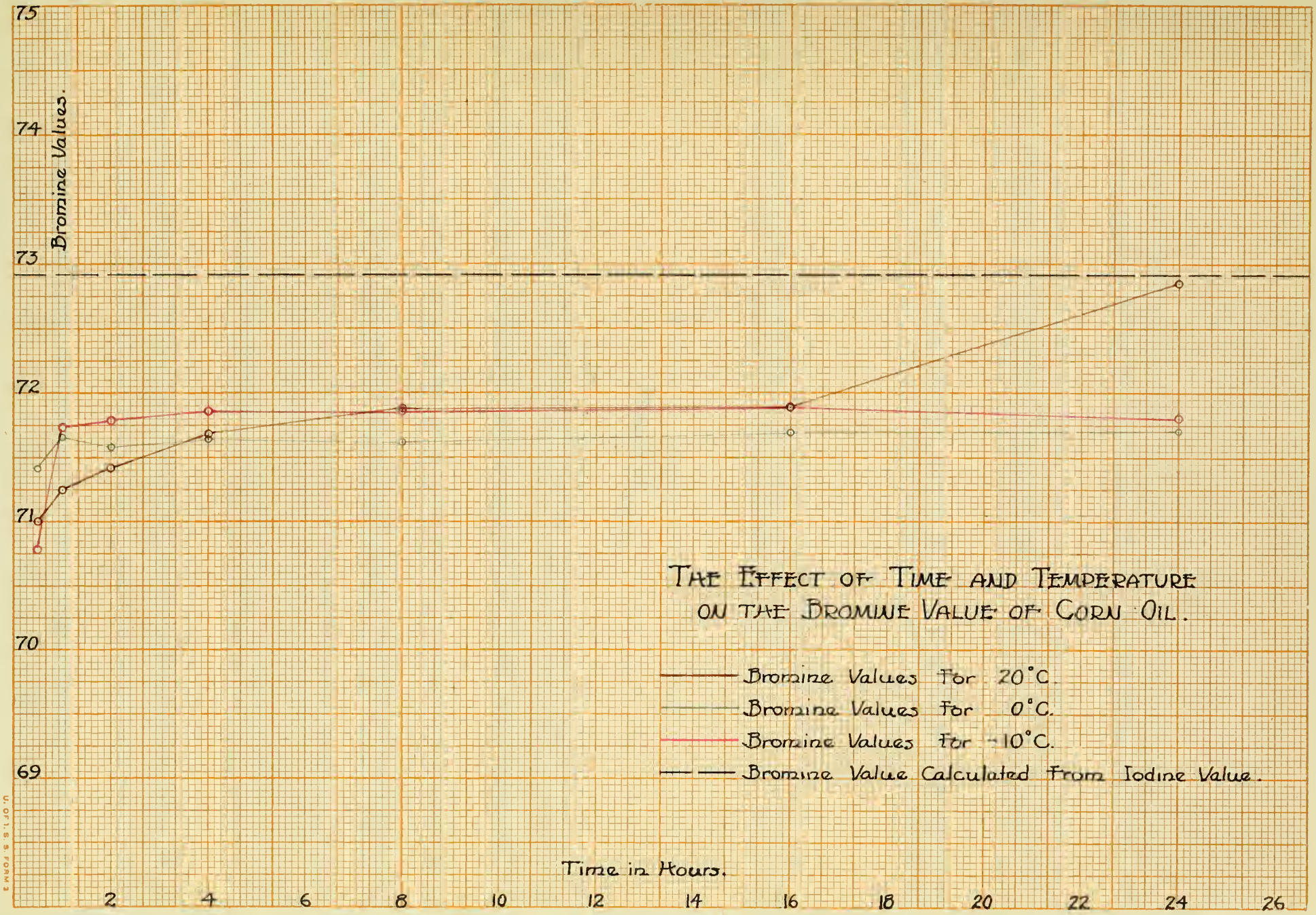
26
Time in Hours.
THE EFFECT OF TIME AND TEMPERATURE
ON THE BROMINE VALUE OF ALMOND OIL.
Bromine Values For 20° C.
Bromine Values For 0° C.
Bromine Values For −10° C.
Bromine Value Calculated From Iodine Value.

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Bromine Values.
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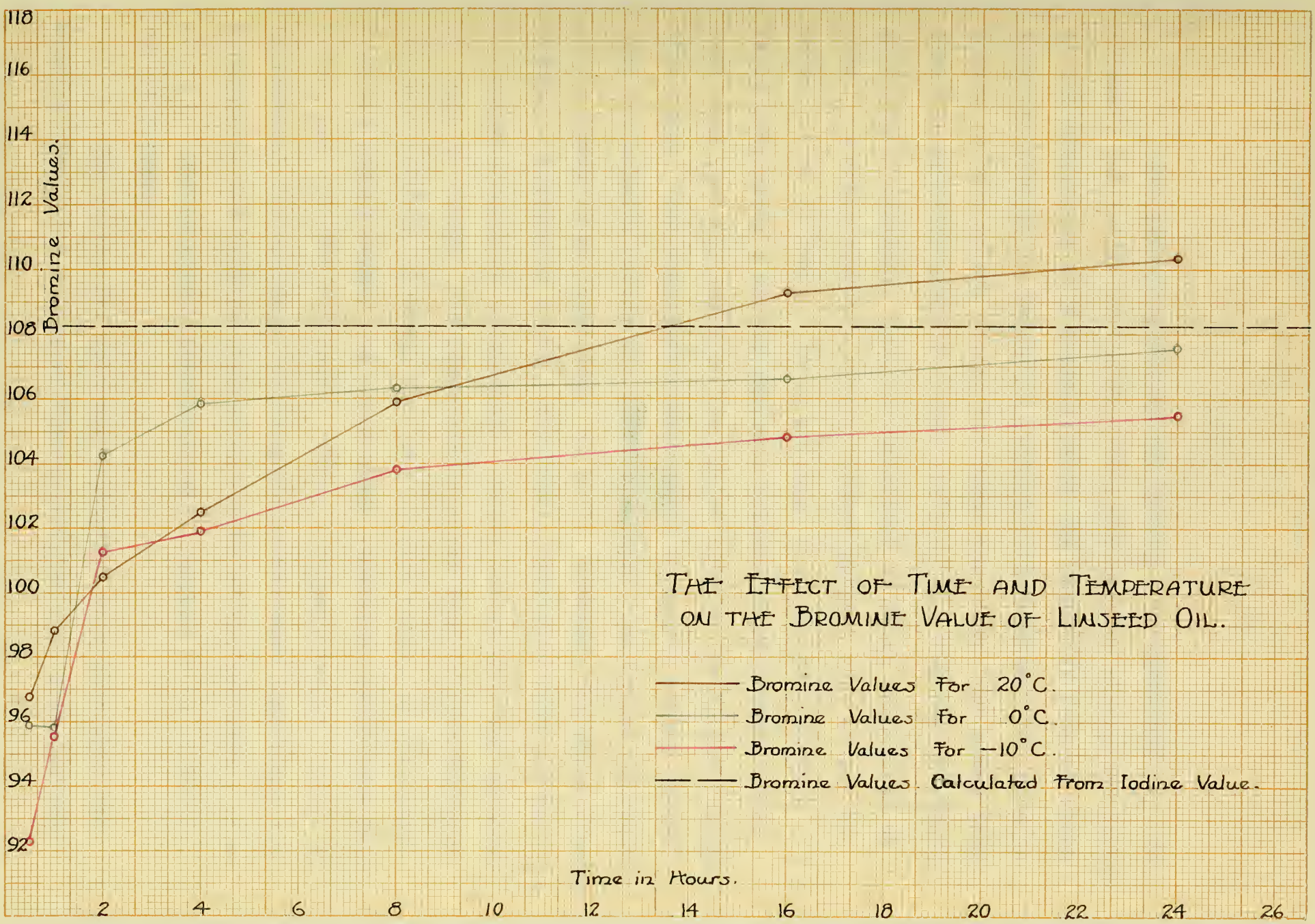
Time in Hours.
THE EFFECT OF TIME AND TEMPERATURE ON THE BROMINE VALUE OF CORN OIL.
Bromine Values For 20°C.
Bromine Values For 0°C.
Bromine Values For -10°C.
Bromine Value Calculated From Iodine Value.



The preceding tables and curves for almond oil are, in general, indicative of the fact that the bromine absorption values of the non-drying oils increase with the length of time in which they are allowed to remain in contact with bromine. The rise in values is very marked during the first two hours, but after that time the reaction seems to reach its limit and the values remain practically constant, with the exception of those determined at 20°C., in which case the bromine number shows a rise of 1.5 between 16 and 24 hours. It is notable that the substitution value also shows a marked increase between these points, which fact very probably explains the sudden rise in the bromine absorption value. The temperature also seems to have a marked effect upon the results during the first two hours, the values increasing as the temperature decreases. At 20°C., however, the value finally reaches a maximum of 63.17, at 24 hours, while at -10° for 24 hours the maximum value is considerably lower, and at 0°C, for 24 hours it falls to 61.32. The lower temperatures seem to give the most constant results, although the true bromine value, as calculated from the iodine number, is found under conditions of 20° for 16.5 hours, and -10° for 8.5 hours. Since a temperature of -10°C., is impractical for ordinary determinations, the best conditions for determining the bromine absorption values of the non-drying oils, using the method herein described, would appear to be at 20° C., for 16.5 hours.

The curves for corn and cottonseed oils show that the bromine absorption values of the semi-drying oils also increase

with time. The increase is most apparent during the first four hours, after which time the values remain rather constant, with the exception of those determined at 20°C., and there again the values rise, showing an increase of from 1.0 to 1.4 between 16 and 24 hours. It is worthy of note that the curves representing the determinations made with corn oil, at the three temperatures are practically equal in value after the first two hours and up to 16 hours, following which time those made at 20°C. show a gradual rise, while the ones made at 0°C. and -10°C., remain practically constant. With cottonseed oil the same is true to all practical purposes, but the values show a slightly greater divergence than do those of corn oil. The true bromine value of cottonseed oil, as calculated from the iodine number, is not reached at 0°C., or -10°C., but is found at 20°C., after approximately 18 hours, while with corn oil the maximum value (obtained after 24 hours at 20°C.) lacks .07 of reaching the calculated bromine value.

The results obtained with linseed oil, as representative of the drying oils, show the greatest uniformity. At the three temperatures a marked increase in the bromine absorption values is found during the first four hours, after which time the values continue to rise, but with much less rapidity. With linseed oil, however, the increasing absorption values seem to be accompanied by a decrease in substitution, which fact leads to the conclusion that the increase is due to continued addition of bromine. The general effect of lowering the temperature is to decrease the bromine

absorption value. The true bromine value of linseed oil is not reached at the lower temperatures but is found at a temperature of 20°C., and 13.5 hours in contact with bromine.

CONCLUSIONS

In general, the bromine absorption values of fats are ultimately increased by prolonged contact with bromine.

The increase is very marked during the first two to four hours (according to the unsaturation of the fat), after which time it remains practically constant, increasing very slightly and very slowly.

The increase in the bromine absorption value with time is also related to the unsaturation of the fat, the less saturated fats showing a more marked rise in absorptive powers than the more saturated ones.

Decreasing the temperature increases the absorptive powers of the more highly saturated fats during the first few hours, but ultimately the absorption values are decreased by the lower temperatures, as compared with the ultimate values obtained with the higher temperatures.

Temperature shows no constant or definite effect upon the absorptive powers of the less saturated fats during the first eight hours, but ultimately the higher temperatures yield the higher values.

Substitution of bromine, in the drying and semi-drying

oils decreases after 16 hours, and any increase in the bromine absorption value thereafter is probably due to continued addition.

Substitution in the non-drying oils increases after 16 hours and any increase in the bromine absorption value thereafter is probably largely due to substitution, rather than addition.

The conditions necessary for determining the true bromine absorption values are as follows:-

(1) With non-drying oils, as represented by almond oil, - 16.5 hours at 20°C.

(2) With semi-drying oils, as represented by corn and cottonseed oils, - 18 hours at 20°C.

(3) With drying oils, as represented by linseed oil,- 13.5 hours at 20°C.

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